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CHROMATOGRAPHIC AND SOLVATOCHROMIC MEASUREMENTS ON BUTYL
RUBBERS

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1.00 AIM

The aim of the present work is to characterise polymers in terms of polymer-solute interactions, and hence to understand solubility properties of the polymers concerned. Sorption, desorption and partition are all important processes that could be better understood with such knowledge of solubility-related interactions.

The two main methods used in this work to characterise polymers are the solvatochromic method, described in the Third Interim Report [1], and the method of multiple linear regression analysis (MLRA) based on linear solvation energy relationship (LSER). It is this latter method that will be described here.

1.10 INTRODUCTION

The LSER equation (1) used in this work comprises of five terms, corresponding to the various processes and interactions that arise between a gaseous probe and a solvent.

$$SP = c + rR_2 + s\pi^H_2 + a\alpha^H_2 + b\beta^H_2 + l\log L^{16} \quad (1)$$

Here $\log SP$ is the logged solubility of a series of gaseous solutes in a particular polymer as a stationary phase. Usually SP is the solute specific retention volume V_G or the gas-liquid partition coefficient, L . The explanatory variables in equation (1) are solute parameters, referring to some particular interaction and are as follows: R is an excess molar refraction, involving interactions of π and n electrons pairs. π the dipolarity/polarisability parameter of dipole-dipole or dipole-induced dipole interaction, α and β

1
1.100 (SOLUBILITY) INTRODUCTION 1

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are hydrogen bond acidity and basicity respectively, and L^{16} is the solute-hexadecane gas liquid partition coefficient, containing both the solute cavity and the general Van der Waals interactions. The constants in equation (1) characterise the complimentary phase properties. Thus r gives an indication of the propensity of the phase to interact with solute π and n electron pairs and is usually positive, except for fluorinated phases. The s constant relates to the interaction of the phase with dipolar-polarisable solutes, the a constant refers to the phase hydrogen bond base and b to the hydrogen-bond acidity (because the basic phase will interact with acidic solutes, and vice versa). The constant l indicates the ability of the phase to separate or to distinguish between homologues in any homologous series.

The characteristic LSER equation (1) and the magnitude of the coefficients will give a measure of the solute-phase interactions. For example a large coefficient in the equation for hydrogen-bond acidity gives an indication of the solute hydrogen-bond acidity. Hence a large s value means that solutes can be separated on the basis of dipolarity, or a large l value shows that separation between homologous series is favourable, and a large a or b value suggest ease of acid and base separation respectively [2].

The data required for the application of equation (1) are gas-liquid partition coefficients, as L , obtained via equation (2) in which ρ is the density of the phase under experimental conditions, and V_G is the specific retention volume of the solute at the column temperature

$$L = V_G \cdot \rho \quad (2)$$

For statistically meaningful results using equation (1), a minimum of 25 retention values of either $\log V_G$ or $\log L$, as $\log SP$, is necessary, covering a wide range of solutes on a given phase. Note that not all the terms in the equation are required if the parameter coefficients are zero or statically insignificant.

2.00 CHROMATOGRAPHIC THEORY

2.10 COLUMN EFFICIENCY

As a solute travels along a column its distribution about the central zone increases in proportion to its migration distance or time in the column [3]. The extent of peak broadening determines the column efficiency, which can be measured as either the number of theoretical plates, n or the height equivalent to a theoretical plate, H or HETP. Assuming the column function of a Gaussian, see fig 1, equation (3) obtains.

$$n = a (t_R/w)^2 \quad (3)$$

Here w_i is defined as the peak width at the inflection point when $a = 4$, w_h is defined as the peak width at half height when $a = 5.54$, and w_b is defined as the peak width at the base when $a = 16$. Alternately the ratio of the peak height to the area of a Gaussian peak can be used to define n

$$n = 2 (t_R \pi h / A)^2 \quad (4)$$

Here h is the peak height and A the peak area. The height equivalent to a theoretical plate is given by the ratio of the column plate count

$$H = L/n \quad (5)$$

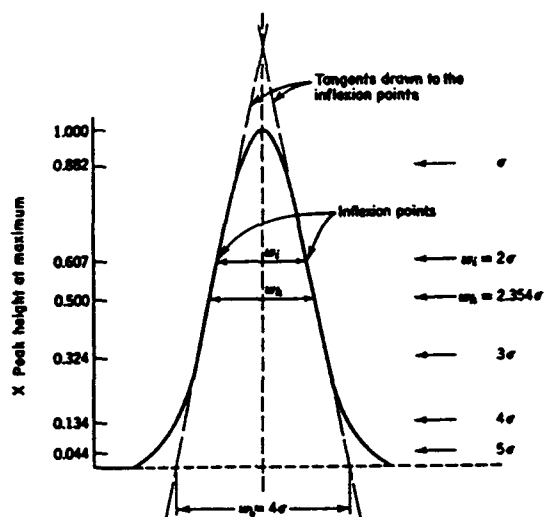


Figure 1. A typical Gaussian peak

Efficiency of the column can also be determined as a number of effective theoretical plates (N) by substituting the adjusted retention ($t_R - t_M$) for the retention time in equation (3). The number of effective plates is often used than the number of theoretical plates since it measures only the band broadening that occurs in the stationary phase. The two measures of column efficiency are related by equation (6). For a low retained time solute, N will only be 25% of the value of n ; however, for higher retained time solute, N and n will be approximately equivalent. N and n are also show reasonably temperature independent.

$$N = n [k / (1+k)]^2 \quad (6)$$

Here k is the ratio of the time spent by the solute in the stationary phase to the time spent in the mobile phase.

$$k = (t_R - t_M) / t_M \quad (7)$$

In the plate model the column can be imagined as being divided up into a number of elementary sections called plate. At each plate the partitioning of the solute with the stationary phase is rapid and in equilibrium before moving on to the next plate. The partition coefficient of the solute is the same in all plates and is assumed to be independent of concentration. The rate of diffusion of the solute in the axial direction along the length of the column is negligible compare with the rate of equilibrium between the mobile and the stationary phase. Axial diffusion is one of the main causes of band broadening, and may be explained by the rate theory.

The plate values vary slightly according to the peak chosen for measurement. They tend to increase with increasing retention volume for the peaks of a homologous series, and often differ for solutes of different functional groups. The types of solute used should be specified and of course the same ones used when columns are compared [4]. The determination of n and N which are dimensionless as a measure of column efficiency are thus very useful.

2.11 RATE THEORY

This theory is based on the continuous nature of the chromatographic process, which is essentially one of diffusion. Account of the diffusion phenomena [3] is taken as follows:

(1) There is resistance to mass transfer between the mobile and the stationary phase, thus preventing the existence of an instantaneous equilibrium. This contributes significantly to band broadening under most practical conditions.

(2) The flow rate through a packed column is irregular, and varies widely with the radial

position in the column. Some molecules will travel more rapidly by following open pathways (channeling); others will diffuse into restricted areas and lag behind the central zone. this process is called eddy diffusion. The difference in flow rates results in dispersion of central zone about the average velocity.

(3) The solute diffuses longitudinally in the gas phase (longitudinally diffusion in the liquid phase is so small it may be ignored), and leads to band broadening that is independent of the flow rate. The diffusion increases as the time spent in the column increases.

The contributions to the band broadening mechanism are considered as independent variables except when specified. The three assumptions above allows a quantitative measure of band broadening contribution due to various factors, and an equation for HETP may be expressed as

$$h = A + B/u + (C_s + C_m)u \quad (8)$$

Here the A term represents the contribution from eddy diffusion, the B term represents the contribution from longitudinal, and the C term represents the contribution from mass transfer in the mobile and stationary phases to the column plate height. If equation (8) is differentiated with respect to the flow rate and the latter then set to be equal to zero, the optimum values of the flow rate (u_{OPT}) and plate height ($HETP_{OPT}$) can be obtained.

$$u_{OPT} = [B / (C_m + C_s)] \quad (9)$$

$$(HETP)_{min} = A + 2 [B (C_m + C_s)]^{1/2} \quad (10)$$

The highest column efficiency, i.e. a minimum value of h , will be obtained at u_{OPT} , see figure 2.

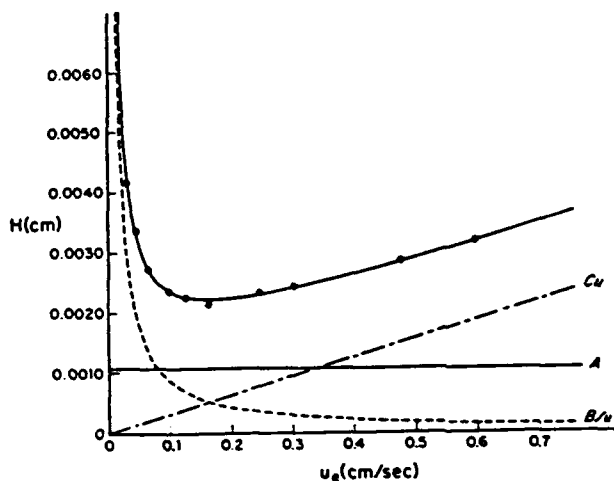


Figure 2. Relationship between band broadening and mobile phase flow rate.

2.20 FACTORS AFFECTING COLUMN EFFICIENCY

Particle size of support. The reduction in size [4] of the particle leads to a reduction in the HETP, i.e. reduction in the peak width. Columns with a fine particle use are less affected by increase of the velocity above the optimum than are columns with a coarse particle use. It is important that the particle size is as uniform as possible, since efficiency is reduced when a wide range is used. The particle size is controlled by the need to remain within limited pressure constraints; this results in the use of column packings of

120-180 μ m in columns less than ca. 5m long.

Carrier gas. The efficiency of the column is less for hydrogen than for heavier gases nitrogen or argon.

Sample size. It is assumed that the total sample is introduced to the column at the start of the chromatogram on the first plate for equilibrium to take place. In fact, the amount of sample is injected is usually much more than the first plate can take, so that it spreads over several, and thus broadens the peak. So the smaller the sample size used the smaller is HETP, and hence for high column efficiency the smallest sample should be used. This seems to contradict the assumption that peak width is independent of sample size, but note however, that such independence of sample size only applies to infinite dilution.

Phase loading. For heavily loaded columns with a liquid phase loading of 25-35% , slow diffusion in the stationary phase film is the main cause of band broadening. With lightly loaded columns (less than 5%) resistance to mass transfer is no longer negligible.

2.30 PEAK SHAPE MODEL

The column is usually assumed to function as a Gaussian operation. In practice, chromatographic peaks are rarely Gaussian, as illustrated in fig. 3, hence departure from the ideal theory may take place.

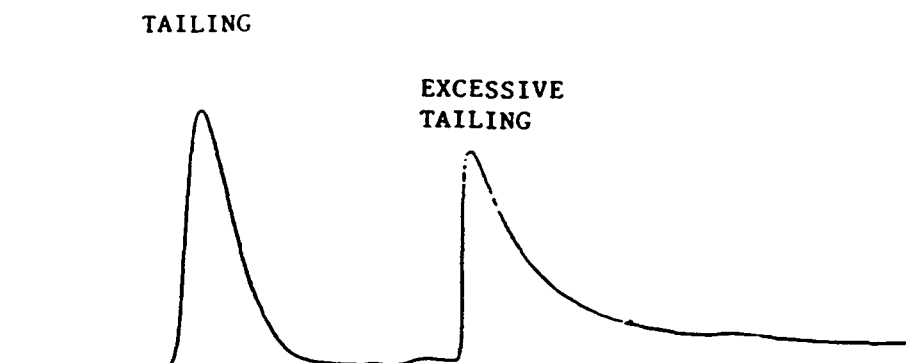


Figure 3. A presentation of peak asymmetry

Peak asymmetry can arise from a variety of instrumental and chromatographic sources. Chromatographic sources include incomplete resolution of sample components, and slow kinetic processes. This corresponds to what has been known as *plug flow*. The influence of slow kinetic processes can be explained by assuming that the stationary phase contains two types of sites. Fast solute exchange between the mobile and the stationary phases occurs at normal sites, and the slow sorption and desorption of solute takes place at the second type. If the time constant for the desorption step of the slow process is greater than half the standard deviation of the peak, then the peak will not only be broadened but will also carry an exponential tail. Examples of slow mass transfer processes include diffusion of the solute in microporous stationary phases.

The asymmetric peak profile data can be extracted by application of digital integration or curve fitting routines[3]. However, many errors and uncertainties may arise from limitations used in the integration, baseline drift, noise and extracolumn contributions from this method of numerical integration. A slight error in determining the baseline will leads to large errors due to the positions of the start and end selected. This is where curve fitting is applied.

3.00 EXPERIMENTAL

All the operation procedures are carried out as described in the First Interim Report [5].

3.10 INSTRUMENTATION

The Gas Chromatography used is a Pye Unicam 104 Series, and the detector attached is a Flame Ionisation (FID).

4.00 RESULTS AND DISCUSSION

The butyl rubbers, 3SSP, B17S and B174 were coated onto chromosorb GAW DMCS inert support, see table 1, as described in the first interim report [5]. Some difficulties were encountered in making up the phase onto the support, due to the high viscosity of these rubbers. As a result a maximum loading of only ca. 5 % could be coated onto the inert support.

For these butyl rubbers, the chromatographic peaks were broad and tailed. The extent of this depends on the functional group. The broad peaks obtained were reduced by increasing the flow rate, aiming for u_{OPT} . Basic functional groups and alcohols all possessed very long tails. This long tail is believed to be due to adsorption of these solutes. Due to a low percentage loading of the phase [6], the gaseous solutes are able to penetrate past the liquid film and interact with the inert support. As a result of peak tailing, the retention data measured were less accurate than usual, as shown by the overall standard deviation in table 4. The larger error in measuring the retention data could be reduced by having a sharper and less diffused peak shape, and this may be obtained by slightly increasing the concentration of the solute than the normal ca. 0.01 μ l. However, it is observed that for alcohols and basic functional groups, when a too large of solutes was injected, the retention data obtained was lower than expected, whilst when a too small volume was injected, the time spent in the column was longer. Therefore, the right volume of solutes used is important in reducing errors. The concentration effect does not apply to aliphatic and aromatic alkanes. The problem of volume concentration was not very obvious in the rubber 3SSP, because most of the volume solute injected were generally larger than for both rubber B17S and B174, where Flame Ionisation Detector (FID) was used, and for the former, Thermal Conductivity Detector (TCD) was used. TCD is less sensitive than FID. The peaks are broad for both TCD and FID.

indicating a low column efficiency. fig. 4 represents a typical peak obtained from these rubbers.



OCTANE



HEXANOL

Figure 4. An example of the type of peaks obtained from butyl rubber B17S.

It is important when using equation (1) to have a wide range of solute parameters as possible. Unfortunately, because of the low basicity of these butyl rubber, it was not possible to use a wide range of solute hydrogen-bond acidity. The key compounds, hexafluoropropan-2-ol and trifluoroethanol were eluted too quickly for accurate measurement even with reasonably long column.

Butyl rubber 388P

For the 43 solutes listed in table 2, a good regression equation was obtained in $\log V_G$ for 3SSP.

$$\text{Log } V_G = -0.920 + 0.07SR_2 - 0.234\pi_2^H + 0.363\alpha_2^H + 1.102 \text{ Log } L^{16} \quad (11)$$

$$N = 43 \quad R = 0.9944 \quad Sd = 0.071$$

As expected, the term in $b\beta^H_2$ is redundant in equation (11), because the butyl rubber 3SSP has zero hydrogen-bond acidity. It can also be deduced from equation (11) that there is very little dipolarity/polarisability present ($s = 0.234$) and very little hydrogen-bond basicity ($a = 0.363$); again this is to be expected from its structure[7]. The most significant term in equation (11) is the $\text{log } L^{16}$, which indicates that the rubber 3SSP interacts with solutes mainly through general dispersion effects. Hence towards specific functionally substituted solutes, the rubber 3SSP appears to be rather inert.

Butyl rubber B178

$$\text{Log } V_G = -1.220 + 0.065R_2 + 0.246\pi_2^H + 0.430\alpha^H_2 - 1.147 \text{ Log } L^{16} \quad (12)$$

$$N = 44 \quad R = 0.9912 \quad Sd = 0.104$$

$$\text{Log } V_G = -1.305 - 0.037R_2 + 0.385\pi_2^H + 0.450\alpha^H_2 + 1.157 \text{ Log } L^{16} \quad (13)$$

$$N = 41 \quad R = 0.9954 \quad Sd = 0.077$$

For the butyl rubber B178, two reasonably good regressions of about 40 solutes was obtained in $\text{log } V_G$ equations (12) and (13), inspite of all the problems with peak broadness, tailing and adsorption. Regression equation of (13) is slightly better than equation (12), because three outlier solutes were eliminated, and they are diiodomethane, triethylamine and dimethylsulphoxide. The dipolarity/polarisability ($s = 0.385$) for equation (13) is slightly larger than the dipolarity/polarisability for equation 12 ($s = 0.246$), while other parameter coefficients are fairly consistant in both equations. It can

be deduced from the above equation, this butyl rubber has again no hydrogen-bond acidity and very little hydrogen-bond basicity. Again the most significant term in equation (12) and equation (13) is the $\log L^{16}$ term, ($l = 1.146$), indicating that the rubber B17S interacts with solutes through general dispersion effects. B17S seemed to be rather inert towards specific functionally substituted solutes. Note, that the rR_2 term is negative in equation (13), but elimination of that term does not affect the overall correlation coefficient, so it is kept in the equation.

Butyl rubber B174

$$\begin{aligned} \text{Log} V_G &= -1.030 - 0.013R_2 - 0.450\pi^H_2 + 0.470\alpha^H_2 + 1.096 \text{Log} L^{16} & (14) \\ N &= 43 & R = 0.9921 & Sd = 0.095 \end{aligned}$$

Again this butyl rubber B174 is shown to have very similar property to the two above rubbers. However, the regression equation (B174) is slightly worse with larger standard deviation. From equation (14), it can be deduced that this rubber (B174) have very little dipolarity/polarisability, ($s = 0.450$) and also very little hydrogen-bond basicity ($a = 0.470$). The main characteristic of this rubber is $\log L^{16}$, indicating a general dispersion interactions between solutes and this rubber (B174). The term in $b\beta_2^H$ is redundant in equation (14), because there is very little hydrogen-bond acidity present, and so statistically insignificant.

The overall view on these three butyl rubbers are that they all have one main feature in common, they interact with solutes through general dispersion effects and very little of either hydrogen-bond acidity, hydrogen-bond basicity or dipolar/polarisability.

5.00 CONCLUSION

The characterisation of the three rubbers, 3SSP, B17S and B174 in terms of polymer-solute interactions using the MLRA method had shown that these polymers have one feature in common. They all interact with solutes through general dispersion effects and very little of dipolar/polarisability or hydrogen bondings. Therefore, it may be concluded that these polymers are inert, thus they are resistant to corrosive or reactive chemicals attack by processes of sorption, desorption or partition as shown by the results obtained. However, it can be said that B17S and B174 have more hydrogen-bond basicity than does rubber 3SSP.

6.00 SOLVATOCHROMIC PARAMETERS MEASUREMENT ON BUTYL RUBBERS

6.10 AIM

To characterise the properties of the polymers using the solvatochromic method, and to compare the results obtained from using two different methods, solvatochromic method and multiple linear regression analysis (MLRA).

6.20 SOLVATOCHROMISM

The solvatochromic principle was first introduced by Kamlet and Taft for determining the β scale for hydrogen bond basicity using the solvatochromic comparison method [8]. The word solvatochromic literally means 'solvent colour'. The principle is based on the phenomenon that the wavelength of maximum absorption (λ_{\max}) of some indicators absorbing in the ultraviolet/visible region of the electromagnetic spectrum, is measurably shifted when the indicators are dissolved in different solvents. The extent of wavelength shift depends on the type and degree of interaction possible between the indicator and the solvent.

The description of how the parameters, π_1 , β_1 and α_1 were arrived at was already mentioned in the Third Interim Report [1]. In brief, α_1 can be calculated from Reichardt's E_T scale of solvent polarity, which also contained solvent hydrogen-bond acidity, as analysed by Kamlet, see equation (15). The solvent scale E_T was first proposed by Reichardt and Dimroth [9] to measure solvent polarity, and is based on the intramolecular charge transfer absorption of

4-(2,4,6-triphenylpyridium)2,6-diphenylphenoxide, Reichardt's dye (Rd), dissolved in a solvent.

$$E_T = 30.2 + 12.35\pi^*_1 + 15.90\alpha_1 \quad (15)$$

E_T is obtained from measurements of λ_{\max} or ν_{\max} for Reichardt's dye, where λ_{\max} or ν_{\max} are in nm.

$$E_T = 28591/\lambda_{\max} \quad (16)$$

7.00 PROCEDURE

Exactly the same procedure is carried out as described in the Third Interim Report [1].

Diagram 1 shows the mechanical spreader that was used to obtain a thin film of polymer.

8.00 RESULTS AND DISCUSSION

The π_1^* values for the three polymers (3SSP, B17S and B174) as set out in table 5, are very close ($\pi_1^* = 0.120$); the values showed that these butyl rubbers have very small dipolarity/polarisability, which as expected value, because of their structure [7]. The β_1 values obtained for these rubbers again show a small hydrogen-bond basicity. From the structure of the butyl rubber, we should not expect any hydrogen-bond acidity, α_1 , as had been shown by the results using MLRA method on LSER, equation (1), where the $b\beta_2^H$ term is rejected for all three rubbers. However, the α_1 values obtained on these rubbers using the solvatochromic method, see equation (15) and (16), showed a significant hydrogen-bond acidity, ($\alpha_1 = 0.730$ for 3SSP, $\alpha_1 = 0.663$ for B17S and $\alpha_1 = 0.688$ for B174). This high value of α_1 can only be due to the presence of moisture present in the rubber as shown in the infra-red spectra at 3500cm^{-1} region. Exhaustive measures had been carried out to get a dry sample, but with no success. The rubbers were placed in an oven for three days at 105°C , but they still showed presence of moisture as can be seen by the infra-spectra taken as dried sample, and thus results in high α_1 values. The b- constant (i.e polymer acidity) obtained chromatographic method is zero, because these rubbers are constantly dried by the flow of dry nitrogen through the column.

Solvatochromic measurements were made on monomer models, chosen to have similar structure to the butyl rubbers; hexane and oct-2-ene, but these were not successful. This is because, the indicator used, Reichardt's dye (Rd) is not not soluble in non-polar solvents, and the second model, oct-2-ene, in which Reichardt's dye is soluble gave a large E_T value, and hence an unreasonably large α value.

9.00 CONCLUSION

The solvatochromic method has shown that both dipolar/polarisability and hydrogen-bond basicity values are small, and the hydrogen bond basicity is slightly larger than the dipolarity/polarisability for all three butyl rubbers. These results are expected. However the hydrogen-bond acidity is much larger than expected, as explained above.

The characterisation of the polymers using the solvatochromic method gives a very quick and easy method of obtaining properties, provided that the polymer is dry and a method is found for keeping the moisture away.

10.00 FINAL CONCLUSION

A comparison between MLRA constants and the solvatochromic parameters is shown in table 9. On MLRA, the polymers B17S and B174 are almost indistinguishable and are both more dipolar/polarisable and have more hydrogen-bond basicity than does rubber 3SSP. From a knowledge [2] of the relationship between s and π_1 , we estimate that a π_1 value of 0.14 corresponds to an s -value of about 0.37, so that the π_1 values are compactible with the experimental s values. However, as mentioned, we prefer the MLRA directly-determined s -values. The α_1 and β_1 values obtained did not correspond to the experimental b and a values from MLRA, so no relationship is established yet.

Results for a number of other rather nonpolar material are collected in Table 10 [10]. It can be seen that the three Butyl rubbers are very close to a sample of poly(isobutylene), investigated previously in this laboratory, obtained from Abraham et al [10]. However, even the rather inert siloxane OV25 has significantly more dipolarity, basicity and acidity than do the butyl rubbers. The MLRA method thus seems to be much more reliable than the solvatochromic method, especially on the determination of phase basicity through the a -constant.

The advantage of using the Solvatochromic method is clear, because it is simple and less time consuming, whereas using the MLRA method is more lengthy.

The disadvantage of using the Solvatochromic method is that the indicator used or the polymer are hygroscopic, thus we need to ensure that the polymer is completely dried before any measurements are made. This can be achieved by taking an Infra-Red spectrum, which would show whether or not moisture is present. For these particular butyl rubbers we were unsuccessful in getting rid of the moisture, and was confirmed by both FTIR and the presence of a very large hydrogen-bond acidity value calculated. Whilst, no such problems were encountered in the MLRA method, this is because the

flow of dried carrier gas would ensure that the polymers (stationary phase) would not be in contact with air, and any traces of moisture in the polymer would be swept dried by the continuous flow of dried nitrogen (carrier gas). It seems that more work is necessary to improve the Solvatochromic method, to ensure that the equations used to calculate the parameters are suitable, and that the prepared sample is moisture free, and the results are absolutely reproducible, which would be if the latter is completely dried. In the mean time both methods would be carried out on the same solvent (polymer) until it is certain that a technique has been found for the Solvatochromic method, that would give a satisfactory result that is reliable.

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Table 1

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[illegible]

Table 2. Absolute values of logVG of butyl rubbers at 298.15K

| COMP NO. | COMPOUND NAME | 388F LogVG | R178 LogVG | R174 LogVG |
|----------|---------------------------|---------------|---------------|---------------|
| 111 | Heptane | 2.516 | 2.303 | 2.178 |
| 126 | Octane | 3.135 a | 2.911 a | 2.972 a |
| 145 | Nonane | 3.724 a | 3.514 a | 3.096 a |
| 180 | Decane | 4.257 | 4.055 | 3.170 |
| 2510 | 1,1,2,2-tetrachloroethane | 3.512 | 3.340 | 3.109 |
| 2540 | 1-chlorobutane | 2.198 | 1.949 | 1.035 |
| 2804 | Trichloroethylene | 2.597 | 2.399 | 2.147 |
| 2835 | tetrachloroethene | 3.249 a | 3.058 a | 3.133 a |
| 3502 | Methyleneiodide | 3.745 | 3.707 | 3.649 |
| 4505 | Butyl ether | 3.477 a | 3.272 a | 3.382 a |
| 4851 | 1,2-Dimethoxyethane | 2.151 | | |
| 5110 | Tetrahydrofuran | 2.091 | 1.939 | 1.947 |
| 5200 | 1,4 dioxane | 2.429 | 2.397 | 2.536 |
| 5503 | Pent-2-one | 2.291 | 2.095 | 2.412 |
| 5512 | Heptan-2-one | 3.477 a | 3.298 | 3.484 a |
| 5535 | Octan-2-one | 3.986 | 3.920 | |
| 5552 | Nonan-2-one | 4.493 | 4.387 | 3.911 |
| 5710 | Cyclohexanone | 3.144 | 3.230 | 3.361 |
| 6003 | Propyl formate | 1.707 | 1.665 | 1.907 |
| 6059 | Pentyl acetate | 3.350 | | 3.206 |
| 6105 | Butyl propanoate | 3.486 | 3.383 | 3.474 |
| 6852 | Diethylamine | 2.204 | | |
| 6902 | Triethylamine | 2.366 | 2.520 | 2.359 |
| 7251 | Dimethylformamide | 2.870 | 2.918 | 3.076 |
| 7261 | NX-dimethylacetamide | 3.519 | 3.450 | 3.640 |
| 8009 | Pentanol | 2.771 | 2.763 | 2.891 |
| 8017 | Hexanol | 3.446 a | 3.365 a | 3.299 |
| 8041 | Heptanol | 3.856 | 3.840 | 3.953 |
| 8071 | Octanol | 4.458 | 4.306 | 4.372 |
| 8192 | Cyclohexanol | 3.326 | | 3.241 |
| 8701 | Dimethylsulphoxide | 4.441 | 2.979 | 3.639 |
| 9112 | Triethylphosphate | 3.460 | 4.649 | 4.474 |
| 10002 | Toluene | 2.890 | 2.741 a | 2.804 |
| 10003 | Ethylbenzene | 3.446 | 3.207 | 3.301 a |
| 10004 | O-Xylene | 3.585 a | 3.466 a | 3.479 |
| 10007 | Propyl-benzene | 3.945 | 3.710 | 3.777 a |
| 10015 | Butylbenzene | 4.401 | 4.398 a | 4.382 |
| 11601 | Chlorobenzene | 3.273 | 3.139 | 3.133 a |
| 11602 | 1,2 dichlorobenzene | 4.234 a | 4.153 | 4.182 |
| 11615 | 4 Chlorotoluene | 3.893 | 3.838 | 3.805 |
| 13601 | Iodobenzene | 4.252 | 4.181 a | 4.277 |
| 15301 | Aniline | 3.803 | 3.710 a | 3.949 |

| | | | | |
|-------|--------------------|---------|-------|---------|
| 16501 | Phenol | 3.760 a | 3.571 | 3.726 a |
| 16503 | m-cresol | 4.260 a | 4.122 | 4.300 |
| 16654 | O-Chlorophenol | 3.922 | 1.018 | 3.983 |
| 16681 | 2,4-dichlorophenol | 2.763 | | |
| 17001 | Benzyl alcohol | 4.182 | 4.068 | 4.218 |
| 19001 | Pyridine | 2.836 | 2.992 | 3.997 |
| 19017 | 3-Ethyl-pyridine | 3.934 | 3.837 | 2.470 |
| 19501 | Pyrolle | 2.484 | 2.372 | |

a Standards used for absolute measurements

Table 3 The parameters of the solutes

| | | σ | $\pi_{H_2}^*$ | $\alpha_{H_2}^*$ | $\beta_{H_2}^*$ | Loc 16 |
|-------|---|----------|---------------|------------------|-----------------|---------|
| 114 | n-Heptane | 0.000 | 0.000 | 0.000 | 0.000 | 3.173 |
| 126 | n-Octane | 0.000 | 0.000 | 0.000 | 0.000 | 3.677 |
| 145 | n-Nonane | 0.000 | 0.000 | 0.000 | 0.000 | 4.182 |
| 180 | n-Decane | 0.000 | 0.000 | 0.000 | 0.000 | 4.686 |
| 2510 | 1,1,2,2-Tetrachloroethane | 0.595 | 0.760 | 0.160 | 0.120 | 3.803 |
| 2530 | 1-Chlorobutane | 0.210 | 0.400 | 0.000 | 0.100 | 2.722 |
| 2804 | Trichloroethene | 0.524 | 0.370 | 0.080 | 0.030 | 2.997 |
| 2805 | Tetrachloroethene | 0.639 | 0.440 | 0.000 | 0.000 | 3.584 |
| 3502 | Diiodomethane | 1.453 | 0.690 | 0.050 | 0.230 | 3.857 |
| 4005 | Di-n-butylether | 0.000 | 0.250 | 0.000 | 0.450 | 3.924 |
| 5110 | Tetrahydrofuran [CH ₂] ₄ O | 0.289 | 0.520 | 0.000 | 0.480 | 2.636 |
| 5200 | 1,4-Dioxane | 0.329 | 0.750 | 0.000 | 0.640 | 2.892 |
| 5503 | Pentan-2-one | 0.143 | 0.680 | 0.000 | 0.510 | 2.753 |
| 5512 | Heptan-2-one | 0.123 | 0.680 | 0.000 | 0.510 | 3.760 |
| 5530 | Octan-2-one | 0.108 | 0.680 | 0.000 | 0.510 | 4.257 |
| 5552 | Nonan-2-one | 0.119 | 0.680 | 0.000 | 0.510 | 4.735 |
| 5710 | Cyclohexanone | 0.403 | 0.860 | 0.000 | 0.560 | 3.792 |
| 6003 | Propyl formate | 0.132 | 0.630 | 0.000 | 0.380 | 2.433 |
| 6110 | n-Butyl propanoate | 0.058 | 0.560 | 0.000 | 0.470 | 3.833 |
| 6402 | Triethylamine | 0.101 | 0.150 | 0.000 | 0.790 | 3.040 |
| 7201 | Formamide | 0.468 | 1.300 | 0.620 | 0.600 | 999.000 |
| 7201 | N,N-Dimethylformamide | 0.367 | 1.310 | 0.000 | 0.740 | 3.173 |
| 7261 | N,N-Dimethylacetamide | 0.363 | 1.330 | 0.000 | 0.780 | 3.717 |
| 8009 | Pentan-1-ol | 0.215 | 0.420 | 0.370 | 0.480 | 3.106 |
| 8017 | Hexan-1-ol | 0.210 | 0.420 | 0.370 | 0.480 | 3.610 |
| 8041 | Heptan-1-ol | 0.211 | 0.420 | 0.370 | 0.480 | 4.115 |
| 8071 | Octan-1-ol | 0.199 | 0.420 | 0.370 | 0.480 | 4.619 |
| 8701 | Dimethylsulfoxide | 0.522 | 1.740 | 0.000 | 0.670 | 3.459 |
| 9112 | Triethyl phosphate | 0.000 | 1.000 | 0.000 | 1.060 | 4.750 |
| 10002 | Toluene | 0.601 | 0.520 | 0.000 | 0.140 | 3.325 |
| 10003 | Ethylbenzene | 0.613 | 0.510 | 0.000 | 0.150 | 3.778 |
| 10004 | o-Xylene | 0.663 | 0.560 | 0.000 | 0.160 | 3.939 |
| 10007 | n-Propylbenzene | 0.604 | 0.500 | 0.000 | 0.150 | 4.230 |
| 10015 | n-Butylbenzene | 0.600 | 0.510 | 0.000 | 0.150 | 4.730 |
| 11601 | Chlorobenzene | 0.718 | 0.650 | 0.000 | 0.070 | 3.657 |
| 11602 | 1,2-Dichlorobenzene | 0.872 | 0.780 | 0.000 | 0.040 | 4.518 |
| 11615 | 4-Chlorotoluene | 0.705 | 0.670 | 0.000 | 0.070 | 4.205 |
| 13601 | Iodobenzene | 1.188 | 0.820 | 0.000 | 0.120 | 4.502 |
| 15301 | Aniline | 0.955 | 0.960 | 0.260 | 0.410 | 3.934 |
| 16501 | Phenol | 0.805 | 0.890 | 0.600 | 0.300 | 3.766 |
| 16503 | m-Cresol | 0.822 | 0.880 | 0.570 | 0.340 | 4.310 |
| 16654 | 2-Chlorophenol | 0.853 | 0.880 | 0.320 | 0.310 | 4.178 |
| 17001 | Benzyl alcohol | 0.803 | 0.870 | 0.330 | 0.560 | 4.221 |
| 19001 | Pyridine | 0.631 | 0.840 | 0.000 | 0.520 | 3.022 |
| 19017 | 3-Ethylpyridine | 0.640 | 0.790 | 0.000 | 0.570 | 4.093 |
| 19501 | Pyrrole | 0.613 | 0.730 | 0.410 | 0.230 | 2.865 |

Table 4. A summary of all the regression equations obtained

| Phase | c | r | s | a | l | n | R | sd | P-statistic |
|-------|--------|--------|-------|-------|-------|----|--------|-------|-------------|
| 388P | -0.920 | 0.078 | 0.234 | 0.363 | 1.102 | 43 | 0.9951 | 0.071 | 958.9 |
| B178 | -1.220 | 0.065 | 0.246 | 0.430 | 1.147 | 44 | 0.9912 | 0.104 | 549.2 |
| B178 | -1.305 | -0.037 | 0.385 | 0.450 | 1.157 | 41 | 0.9954 | 0.077 | 969.1 |
| B174 | -1.030 | -0.013 | 0.450 | 0.474 | 1.096 | 43 | 0.9921 | 0.095 | 590.4 |

n : no. of solutes
R : overall correlation coefficient
sd : standard deviation

TABLE 7 ABSORPTION MAXIMA FOR DYES IN POLYMER

| POLYMER | $N1, \lambda$ | $N2, \lambda$ | Rd, λ |
|---------|---------------|---------------|---------------|
| | nm | nm | |
| 388P | 361.58 | 333.47 | 661.5 |
| B178 | 361.05 | 334.00 | 676.2 |
| B174 | 361.18 | 332.95 | 670.9 |

TABLE 8 SOLVATOCHROMIC PARAMETERS FOR POLYMER

| POLYMER | π_1 | β_1 | α_1 |
|---------|-------------------|-------------------|---------------------|
| 388P | 0.147 ± 0.011 | 0.151 ± 0.015 | (0.730 ± 0.013) |
| B178 | 0.137 ± 0.011 | 0.171 ± 0.015 | (0.663 ± 0.013) |
| B174 | 0.140 ± 0.011 | 0.144 ± 0.015 | (0.688 ± 0.013) |

TABLE 5 CONCENTRATION USED FOR POLYMER SOLUTION

| POLYMER | M.W | WEIGHT OF POLYMER (g) | VOLUME OF SOLVENT |
|---------|-----------|--------------------------|----------------------|
| 388P | 1,300,000 | 14.89 | 100 |
| B178 | 1,300,000 | 15.09 | 100 |
| B174 | 1,300,000 | 15.10 | 100 |

TABLE 6 CONCENTRATION USED FOR INDICATOR SOLUTION

| INDICATOR | M.W | WEIGHT (g) | VOLUME (ml) |
|----------------------------------|--------|---------------|----------------|
| N,N-dimethyl-p-nitroaniline (N1) | 166.00 | 0.0125 | 5 |
| P-nitroaniline (N2) | 138.00 | 0.0090 | 5 |
| Reichardt's dye (Rd) | 551.69 | 0.0090 | 5 |

Table 9 Comparison of MLRA and Solvatochromic results

| POLYMER | MLRA | SOLV | MLRA | SOLV | MLRA | SOLV |
|---------|------|---------|------|-----------|------|------------|
| | s | π_1 | a | β_1 | b | α_1 |
| 388P | 0.23 | 0.15 | 0.36 | 0.15 | 0.00 | (0.73) |
| B178 | 0.38 | 0.14 | 0.45 | 0.17 | 0.00 | (0.66) |
| B174 | 0.45 | 0.14 | 0.47 | 0.14 | 0.00 | (0.69) |

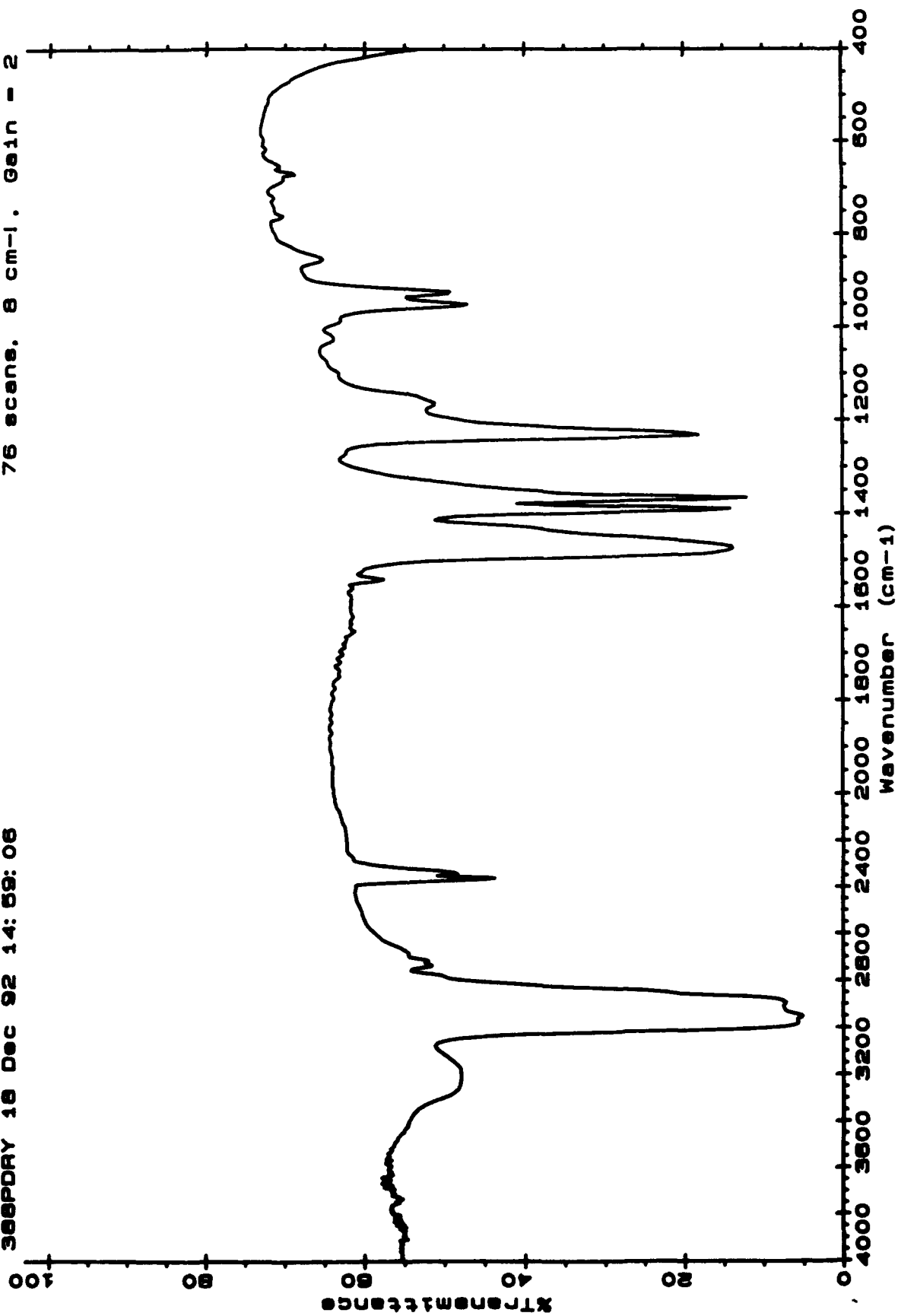
Table 10 Comparison of MLRA results for Butyl rubbers with
other materials at 298K

| POLYMER | r | s | a | b | l |
|------------------------------|-------|------|------|------|-------|
| 388P | 0.08 | 0.23 | 0.36 | 0.00 | 1.102 |
| B178 | -0.04 | 0.38 | 0.45 | 0.00 | 1.157 |
| B174 | -0.01 | 0.45 | 0.47 | 0.00 | 1.096 |
| Polyisobutylene | -0.08 | 0.37 | 0.18 | 0.00 | 1.016 |
| Poly(methylsiloxane) OV25 | 0.18 | 1.29 | 0.56 | 0.44 | 0.885 |
| Hexadecane | 0.00 | 0.00 | 0.00 | 0.00 | 1.000 |

FTIR SPECTRUM OF BUTYL RUBBER (3SSP) DRIED AT 108°C

388PDRY 18 Dec 92 14:59:06

76 scans, 8 cm⁻¹, Gain - 2

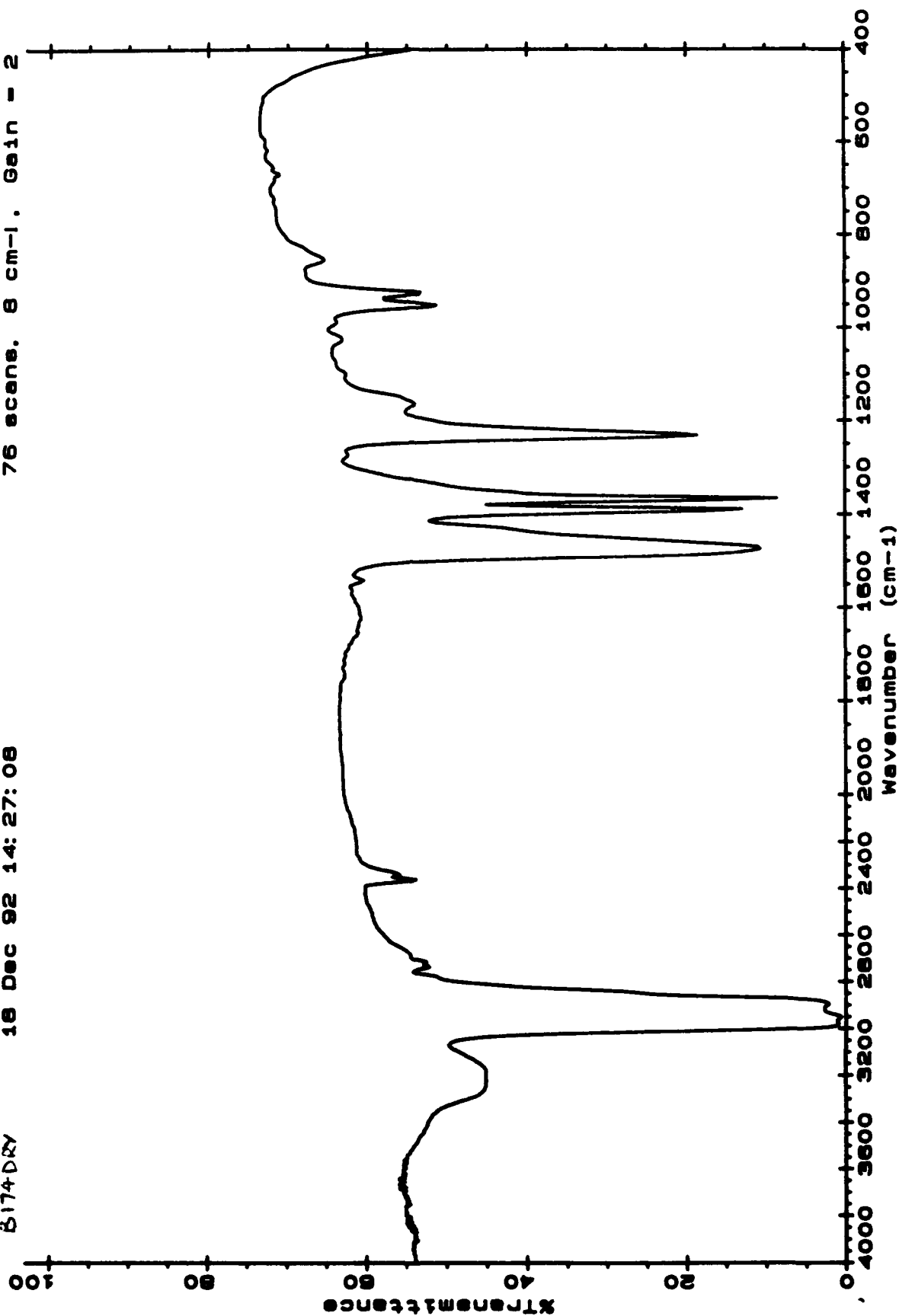


FTIR SPECTRUM OF BUTYL RUBBER (B174) DRIED AT 105°C

B174 DRY

18 Dec 92 14:27:08

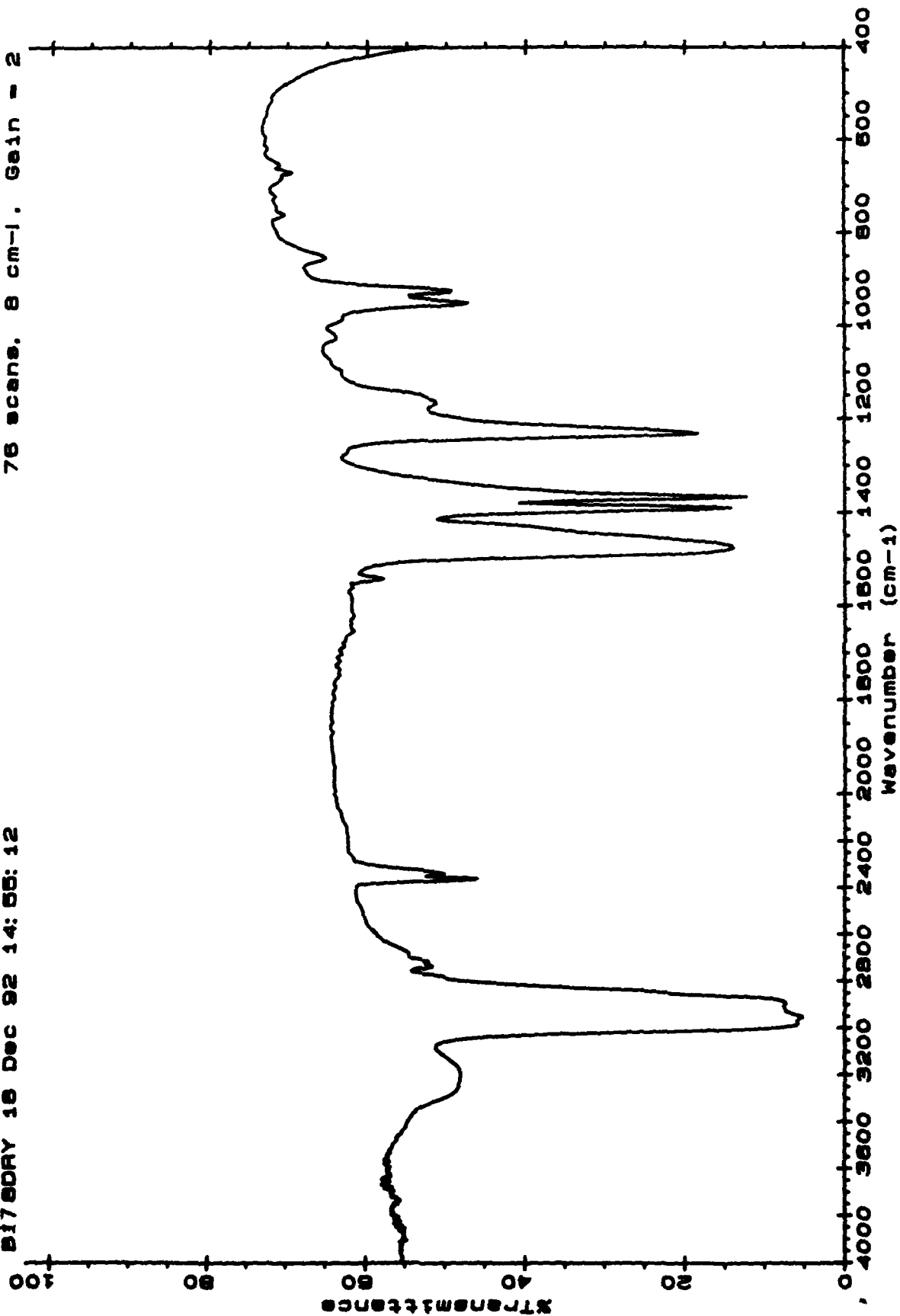
76 scans. 8 cm-1. Gain - 2



FTIR SPECTRUM OF BUTYL RUBBER (B178) DRIED AT 100°C

B178DRY 18 Dec 92 14:55:12

76 scans, 8 cm-1, Gain = 2



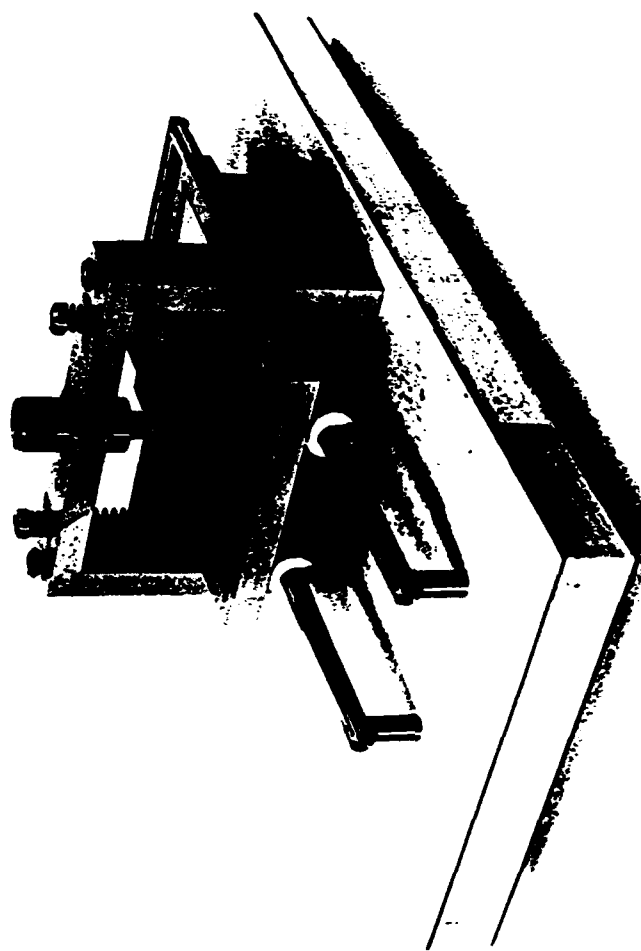


Figure 1 A mechanical spreader